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Computer-aided simulation of the influence of collective effects on polymer-melt dynamics in a straight cylindrical tube: Observation of the onset stage of the corset effect

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Abstract

The results of the computer-aided simulation of the dynamics of a polymer melt consisting of Fraenkel chains in straight cylindrical tubes and in bulk are discussed. Two different models are studied. In the first model, the dynamics of the polymer melt is simulated via the molecular dynamics simulation. The interaction of unbound polymer segments is described by the Lennard-Jones potential, which excludes any chain crossing of macromolecules and generates collective acoustic waves. In the second model, which serves as a reference, the system is studied via the Brownian dynamics method, in which intermolecular interactions are allowed for phenomenologically via friction and stochastic Langevin forces. In this case, cooperative effects are absent and the effect of spatial confinements makes itself evident only in a narrow near-wall layer. For the two models under consideration, there is a significant difference in the decay of dynamic correlation functions C αβ = {b α(t)b β(t) α(0)b β(0)}(b 2 αb 2 β) -1, where averaging is performed over all macromolecular segments and b α (t) is the α component of the end-to-e-d-segment vector (α = β = x,y, and the cylindrical axis of the tube is directed along the z axis). For the first model allowing for collective effects, the dynamics of decay C αβ(t) of functions is much slower than that for the melt in bulk, and for the second model, in which the presence of the tube leads only to spatial confinements for the polymer segments in the direct vicinity of walls. This difference indicates the fundamental significance of the collective effects in the dynamics of poly- mer melts confined in porous media. This phenomenon is the first computer-simulated evidence of the onset stage of the so-called corset effect, which was first observed experimentally with the use of NMR relaxometry. © Pleiades Publishing, Ltd., 2012.

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